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1st Technical Report

Jan 1 - July 31, 1971

"Studies of Electron States in Structurally Disordered Materials Using Simple Liquids and Dense Vapors as Prototypes."



## Summary

During the first six months of this grant we concentrated on the theoretical aspects of the problem. (The experimental phase involved primarily the setting up of apparatus). Three problems were investigated and these were: 1) Monte Carlo calculations of transient photocurrents; 2) Electron drift in very dense helium; and 3) Electronic structure of a one dimensional disordered array of δ-function potential.

Using a simplified Monte Carlo approach we have been able to calculate the main features of the experimentally observed transient photocurrent in amorphous selenium and arsenic triselenide. We included in this calculation surface trapping and release as well as bulk trapping and release.

Following the recently published calculations of Eggarter and Cohen,[1] we have begun a calculation on the temperature and density dependence of the drift mobility of electrons in very dense helium. To date our calculations are in agreement with the data of Harrison and Springett[2] over a temperature range of 4°K to 18°K.

We have applied the Wu-Dy[3] method to calculate the density of states for an electron in a one-dimensional disordered array of attractive δ-function potentials. The results are in excellent agreement with those obtained using

the node-counting method of Lax and Phillips.[4] Our method has the advantage in that it can easily be extended to three-dimension.

## Methods and Results

The general methodology and results of the works summarized above are given in the following three sections:

I. Monte Carlo Calculations of Transient Photocurrents

The detailed description of this work is contained in two papers, one is published in the Phys. Rev. Letters 27, 21 (1971), the other was reported at the Fourth International Conference on Amorphous and Liquid Semiconductors. (The conference proceedings will be published in the Journal of Non-Crystalline Solids.) Both these papers are attached below for reference.

II. Mobility of Excess Electrons in Helium Gas -- Density and Temperature Dependence.

The recent theory of Eggarter and Cohen[1] was used to calculate the mobility of excess electrons in dense helium gas as a function of gas density and temperature. The results were then compared with recent experimental measurements of Harrison and Springett.[2]

The low field mobility was obtained from[1]

$$\mu(p,T) = \frac{\int \mu(E)\, n(E)\, e^{-E/kT}\, dE}{\int n(E)\, e^{-E/kT}\, dE}$$

and displayed in Fig. 1 as best fits to the experimental results along with calculations designed to show the sensitivity of the theory to the adjustable parameter c.[1] It should be pointed out that only for $\mu < 1$ $cm^2 sec^{-1} V^{-1}$ were there any appreciable contributions due to the motion of trapped electrons. The mobility drop with density is due to the decrease of the number of electrons in extended states.

As can be seen the density dependence of the mobility is in good agreement with experiment except for the over estimate at the low density region shown due to neglect of scattering by clusters of atoms smaller than the rms deviations from the average number of atoms in each cell.[1] The temperature dependence is forced to agree by the variation in c.

These calculations will be extended to include the Hall effect and the high electric field regime.

## III. Electronic Structure of a One-dimensional Disordered Array of δ-function potential.

In our calculation, we considered arrays having short range order as defined by Gubanov in the following way: The distance between each pair of neighboring atoms is taken to be $a(1 + \varepsilon\gamma)$, where a is the average interparticle spacing, $\varepsilon$ is a positive number less than one (called the short range order parameter) and $\gamma$ is a random number having a Gaussian distribution with $\langle\gamma\rangle = 0$, and $\langle\gamma^2\rangle = 1$.

The Hamiltonian we consider is given by

$$H = \frac{p^2}{2m} - \sum_{\ell} V_o \delta(x - \ell)$$

where $V_o$ is a positive number which defines the strength of the potential and $\ell$ denotes the atomic sites. The tight-binding wavefunction is taken to be the eigenstate

$$\varphi_\ell = \frac{mV_o}{\hbar^2} \exp\left(-\frac{mV_o}{\hbar^2}|x - \ell|\right)$$

of

$$h_\ell \equiv \frac{p^2}{2m} - V_o\delta(x - \ell)$$

with eigenvalue

$$w = -\frac{mV_o^2}{2\hbar^2} .$$

For simplicity we set w equal to -1. Using $\varphi_\ell$ one easily computes for the

matrix elements of the total Hamiltonian:

$$H_{\ell\ell'} = w\delta_{\ell\ell'} + 2w \sum_{\ell''\neq\ell} \exp\{-\frac{A}{a}(|\ell'' - \ell| + |\ell'' - \ell'|)\}$$

where

$A \equiv \frac{mV_o}{\hbar^2} a$, defines the degree of overlap of the wave functions. Using $H_{\ell\ell'}$, we calculated the following quantities needed in the Wu-Dy[3] method: $\tilde{V}(k)$, $U(\ell,k)$, $R_{kk'}$ and $\tilde{W}_{kk'}$. We then calculated the Greens function using the direct summation of the band propagator expansion:

$$\langle\tilde{G}(k,z)\rangle = \frac{1}{z - \tilde{V}(k) - \langle\Sigma(k,z)\rangle_c}$$

where

$$\langle\Sigma(k,z)\rangle_c = \langle\tilde{W}_{kk}\rangle_c + \sum_{k'}\langle\tilde{W}_{kk'}\langle\tilde{G}(k',z)\rangle\tilde{W}_{k'k}\rangle_c + \ldots$$

and $\langle\ \rangle_c$ is the cummulant average. We truncated the series for the proper self-energy $\Sigma$ at the second term and solve for $\tilde{G}$ selfconsistently. The density of states is then calculated from $\tilde{G}$ by

$$n(E) = \frac{1}{\pi} \sum_k I_m\langle\tilde{G}(k,z \to E + i0^+)\rangle .$$

In the following Fig.2 we show the integrated density of states N(E), i.e., the number of states with energy less than E, for the case of $\varepsilon = 0.05$ and $A = 10$. The calculation was carried out with 30 particles and averaged over 20 randomly chosen configurations. The figure shows clearly the detail of the band tail and the agreement with the node-counting method is excellent. Investigation of systems with larger degree of disorder and the effect of the truncation of the self-energy series is now in progress.

## References

1. T. P. Eggarter and M. H. Cohen, Phys. Rev. Letters 27, 129 (1971), also see their work in Phys. Rev. Letters 25, 807 (1970).

2. H. R. Harrison and B. E. Springett, Phys. Letters 35A, 73 (1971).

3. K. S. Dy and S. Y. Wu, Phys. Rev. B3, 1173 (1971).

4. M. Lax and J. C. Phillips, Phys. Rev. 110, 41 (1958).

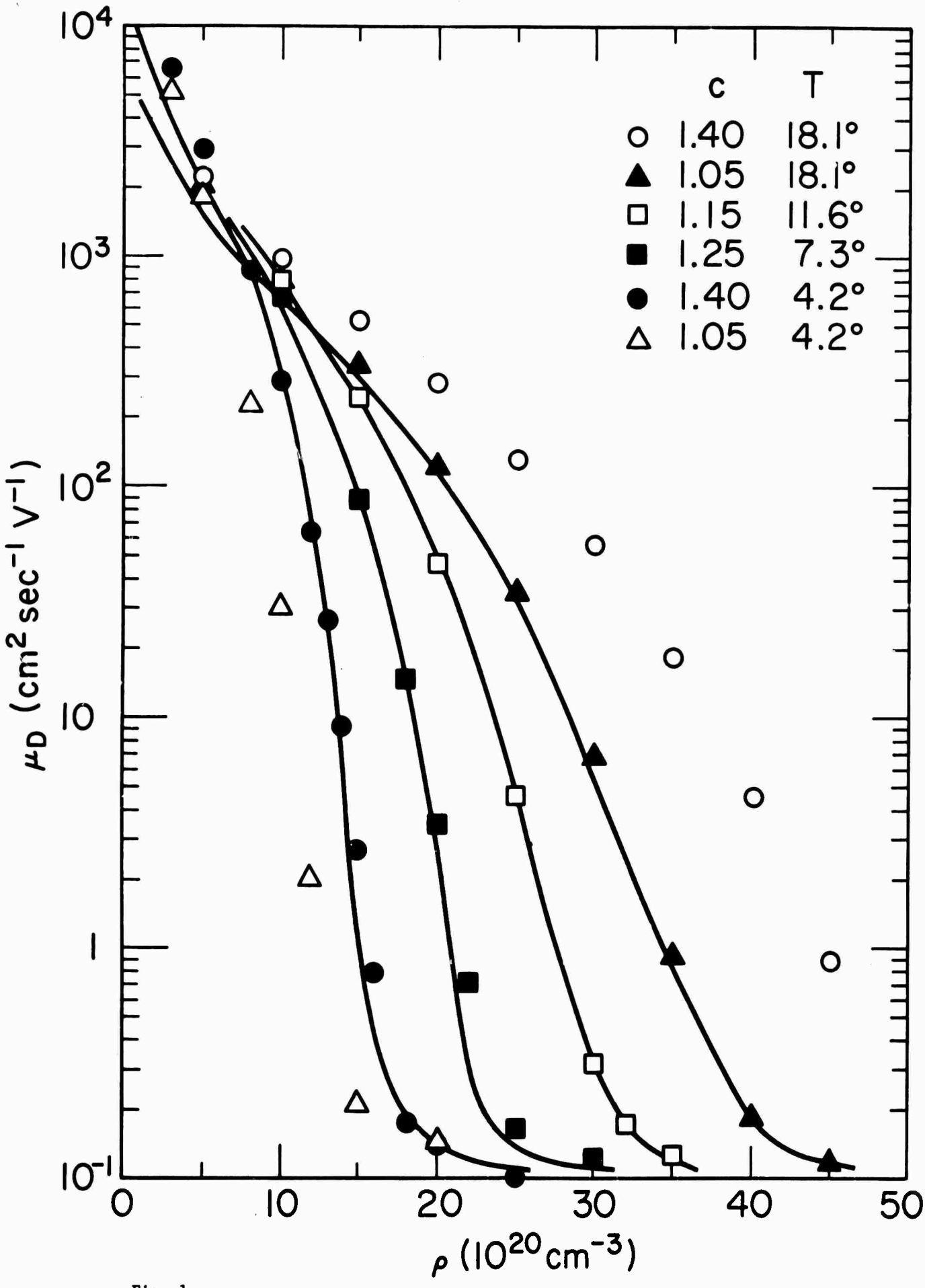
c T
1.40 18.1°
1.05 18.1°
1.15 11.6°
1.25 7.3°
1.40 4.2°
1.05 4.2°
$\mu_D$ (cm$^2$ sec$^{-1}$ V$^{-1}$)
$\rho$ ($10^{20}$ cm$^{-3}$)
$10^4$
$10^3$
$10^2$
10
1
$10^{-1}$
0
10
20
30
40
50

Fig. 1

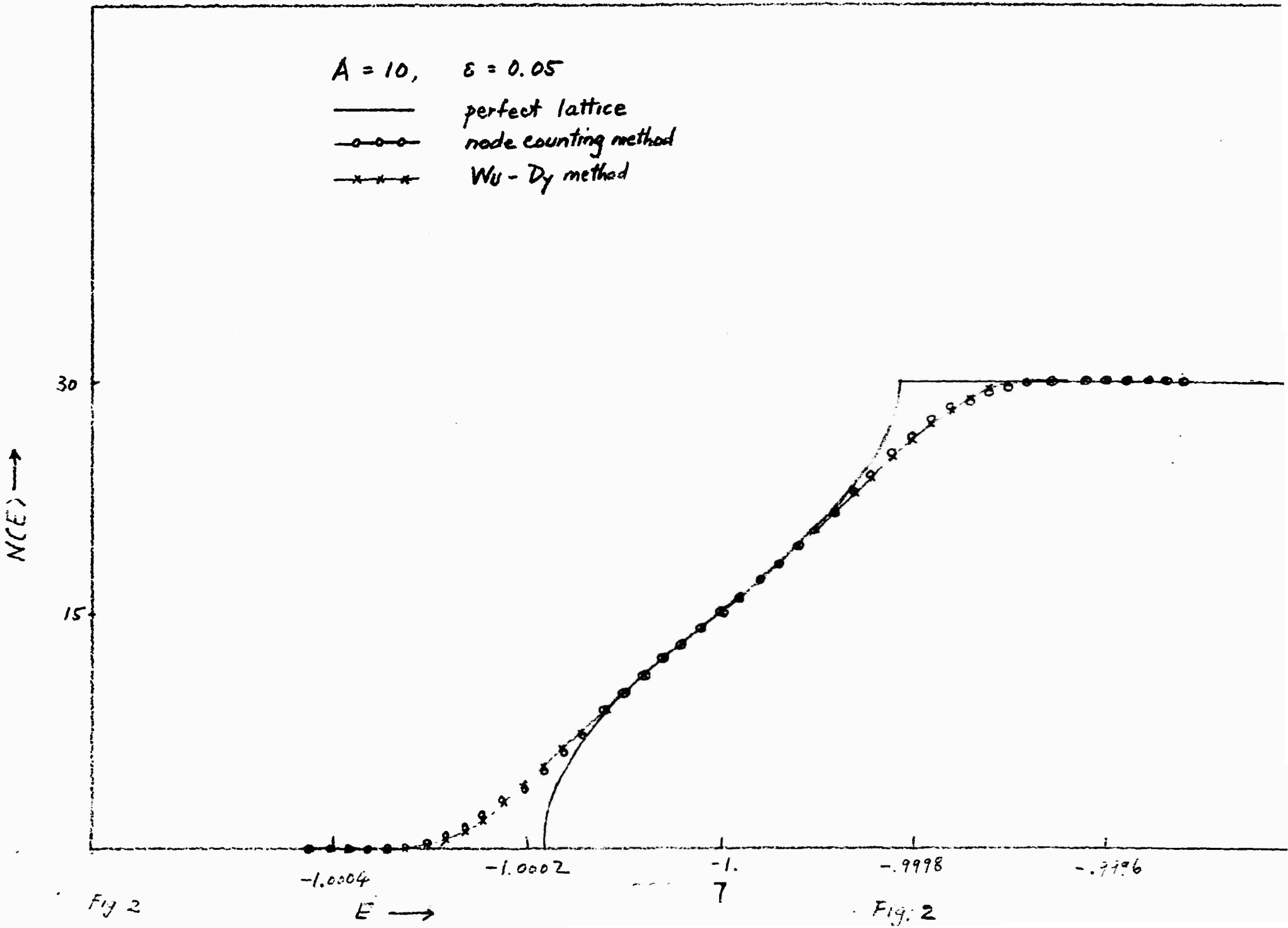
A = 10, ε = 0.05
perfect lattice
node counting method
Wu - Dy method
30
15
N(E) ⟶
-1.0004
-1.0002
-1.
-.9998
-.9996
E ⟶

Fig 2



Fig. 2

# Monte Carlo Calculation of Transient Photocurrent in Low Carrier Mobility Materials*

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## ABSTRACT

A Monte Carlo method is used to calculate the shape of the transient photocurrent under flash excitation. It is shown that some of the anomalous features of the experimental data can be explained by including surface as well as bulk trapping in the model. In particular, this simple picture predicts the observed long tail of the pulse as well as the apparent field dependence of the mobility.

*Work supported by the Army Research Office of Durham and the Material Research Center, under Contract No. SD-100 with the Advance Research Project Agency.

In recent years transient photocurrents have been examined very successfully in low mobility material. Our present day understanding of the electronic properties of organic[1] and molecular[2] crystals and amorphous semiconductors[3] result largely from interpretation of such experiments. In addition to obtaining information on drift mobilities, data on trapping cross-sections were also obtained.

One problem persisted however and that was that the theoretical pulse shape was not always observed even in the same material. Typical photocurrents are shown in figure 1. There we show in figure 1A a curve obtained from anthracene which closely resemble the theoretical pulse shape. Figure 1B shows another pulse obtained from anthracene with a different electrode. Finally figure 1C shows a typical pulse obtained from $As_2Se_3$. Noticeable in figure 1B and 1C are very long tails after a break in the curve which ostensibly represents the transit time.

This long tail prompted M. E. Scharfe[4] to suggest that it was due to a dispersion in the arrival time of the carriers due to a distribution of mobilities. This interpretation seemed physically unsound because it implies that different carriers sample different density of states or different traps. This would be equivalent to having parallel strips of different materials.

We propose a different and physically more sound model and that is that the generated carriers in addition to being trapped in the bulk may also be trapped at the illuminated surface. The surface trapping is equivalent to a delay in the carrier generation.

In order to illustrate that such a simple process can give the desired pulse shape, we further simplify the model by assuming that there is only

one trapping level in the bulk and only one level at the surface. It is not significantly more difficult to include a distribution of levels and even surface recombination. (Calculations including these cases are presently being undertaken.)

In order to calculate the current pulse we have chosen to use a simplified Monte Carlo approach rather than solve the continuity of current equation. We took this approach because we wanted to make as few mathematical assumptions and approximations as possible.

In the Monte Carlo approach we only have to choose a trapping probability and an escape probability. We do not have to be concerned with equilibrium between the trapping states and the conduction band at any time from t = o to t = ∞. Any approach to equilibrium will automatically come about through the statistics.

This calculation is extraordinarily simple. One first chooses a surface trapping probability and this is just $N_D/(N_D+N_I)$ where $N_D$ is the number of carriers trapped at the surface, and $N_D + N_I$ is the total number of carriers.

The $N_I$ carriers are instantaneously injected into the bulk and using a set of random numbers we can follow the history of each one. The sequence of events are:

| | |
|---|---|
| first trapping time : | $t_T(1) = -\tau_\alpha \ell n\, r_T(1)$ |
| first emptying time : | $t_e(1) = -\tau_\beta \ell n\, r_e(1)$ |
| . . . . . | . . . . . |
| nth trapping time : | $t_T(n) = -\tau_\alpha \ell n\, r_T(n)$ |
| nth emptying time : | $t_e(n) = -\tau_\beta \ell n\, r_e(n)$ |

where $\tau_\alpha$ and $\tau_\beta$ are the characteristic trapping time and emptying time for bulk traps. This sequence is continued until $\sum_{n=1}^{m} t_T(n) = t_o/y$, where $t_o/y$ is the transit time (y is a parameter which plays the role of the applied voltage and $t_o$ is a fixed constant). The trapping time for the final event $t_T(m)$ usually has to be cut short to make the sum exactly equal to $t_o/y$. The values of $r_T(n)$ and $r_e(n)$ are random numbers generated by a computer. By following each particle we can tell at any time how many are free and the sum of these is proportional to the current.

The procedure for the $N_D$ particles is the same as for the $N_I$ particles except that the first event is a surface trap emptying one with a distribution of emptying times given by $t_s(1) = -\tau_\gamma \ell n r_s(1)$, $\tau_\gamma$ being the characteristic release time for surface traps. Figure 2 shows a set of the results for the number of free carriers at a given time t plotted against yt for $N_I = 1000$, $N_D = 7000$, and y = 0.1 through 2.5. In all cases, we have chosen the values $\tau_\alpha = \tau_\gamma = 4 \times 10^{-4}$ secs, $\tau_\beta = 10^{-3}$ secs and $t_o = 10^{-3}$ secs. We see that only at high voltages does one get a break in the curve at $yt = t_o$. Further, it had previously been assumed that by measuring the decay of the current before the break one could obtain information on the trapping time. As can be seen neither $t_o$ nor $\tau_\alpha$ are derivable by such simple procedures as observing the decay and the break point.

Finally one can plot the reciprocal of the apparent transit time (the break point $t_B$) versus the applied voltage. These results are shown in figure 3. There is an apparent field dependent mobility which is nothing more than a transition from the trap controlled to the trap free case with increasing voltage. This curve is very similar in shape to

that obtained by Tabak[3] who postulated a field dependent mobility to explain the results.

We conclude from these calculations that the so called complicated drift experimental results obtained on amorphous materials such as $As_2Se_3$ may in fact be very simple and involve well known processes. Further, to derive the mobility and the trapping times one must study the current pulses in detail as a function of field and temperature.

## References

1. O. H. LeBlanc, Jr., Physics and Chemistry of the Organic Solid State, Vol. III, D. Fox, M. M. Labes, A. Weissberger, Eds., Interscience Publishers, 1967, pp. 133-198.

2. A. Many and G. Rakavy, Phys. Rev. 126, 1980 (1962).

3. M. D. Tabak, Phys. Rev. B2, 2104 (1970).

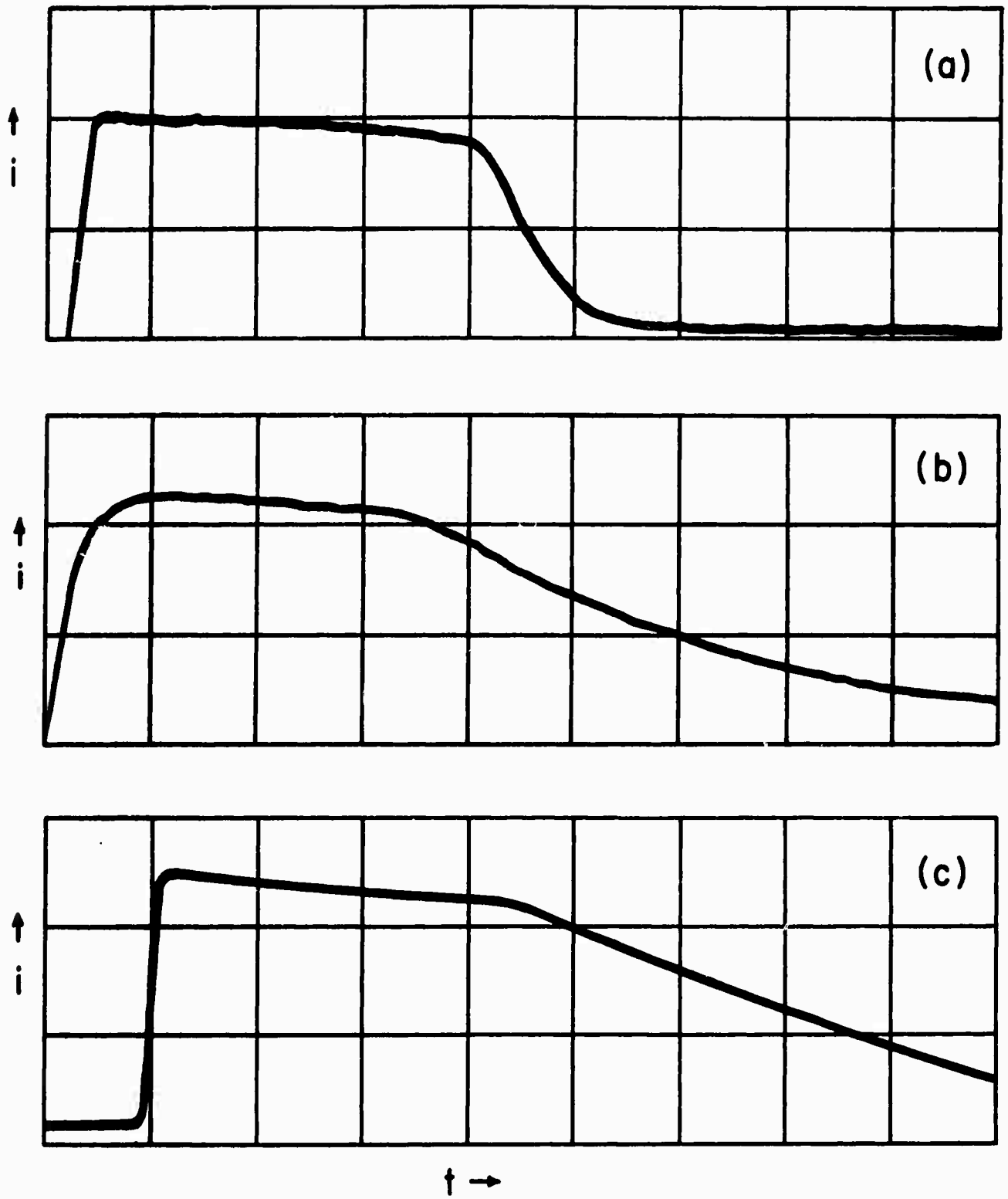
4. M. E. Scharfe, Phys. Rev. B2, 5025 (1970).

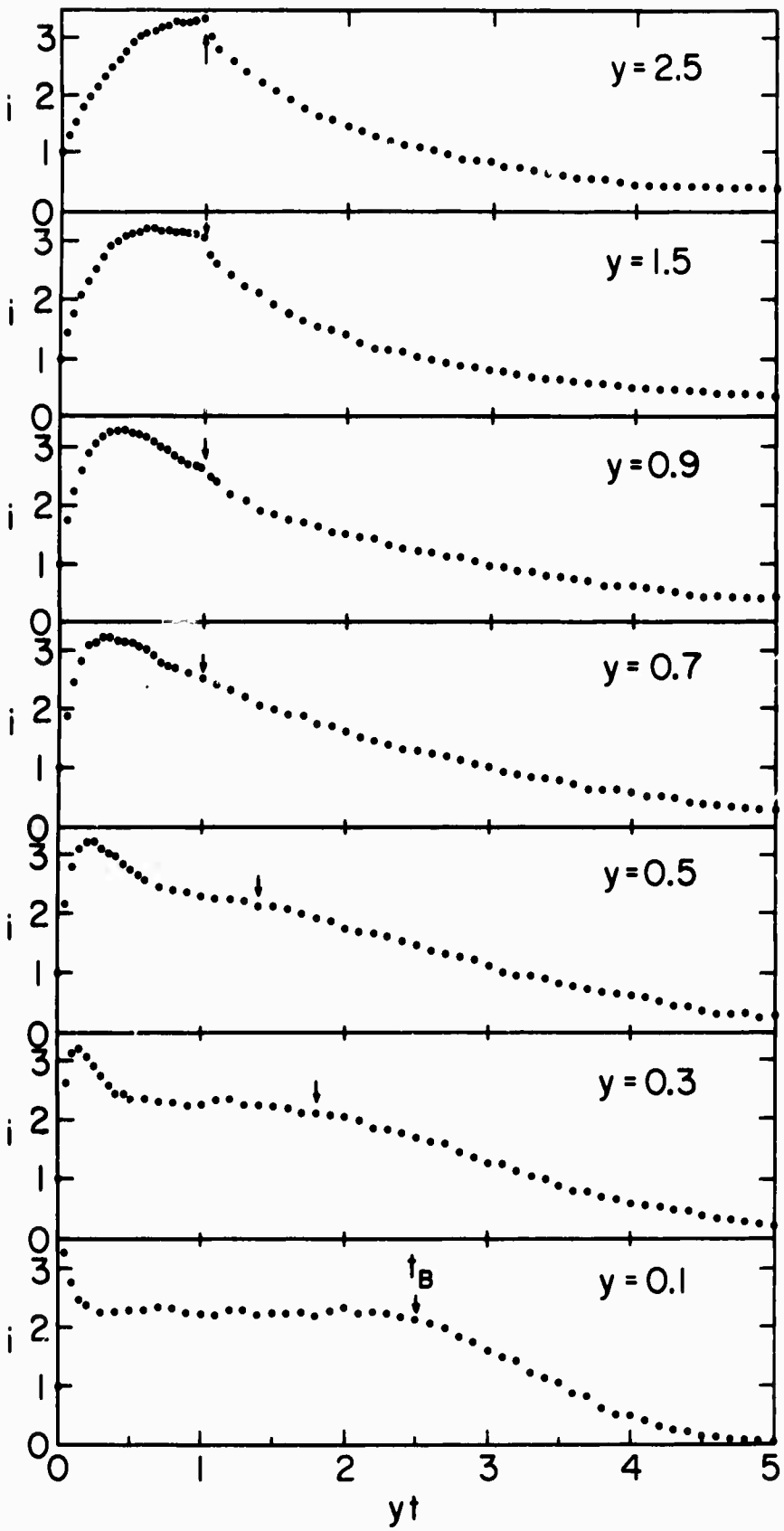
## Figure Captions

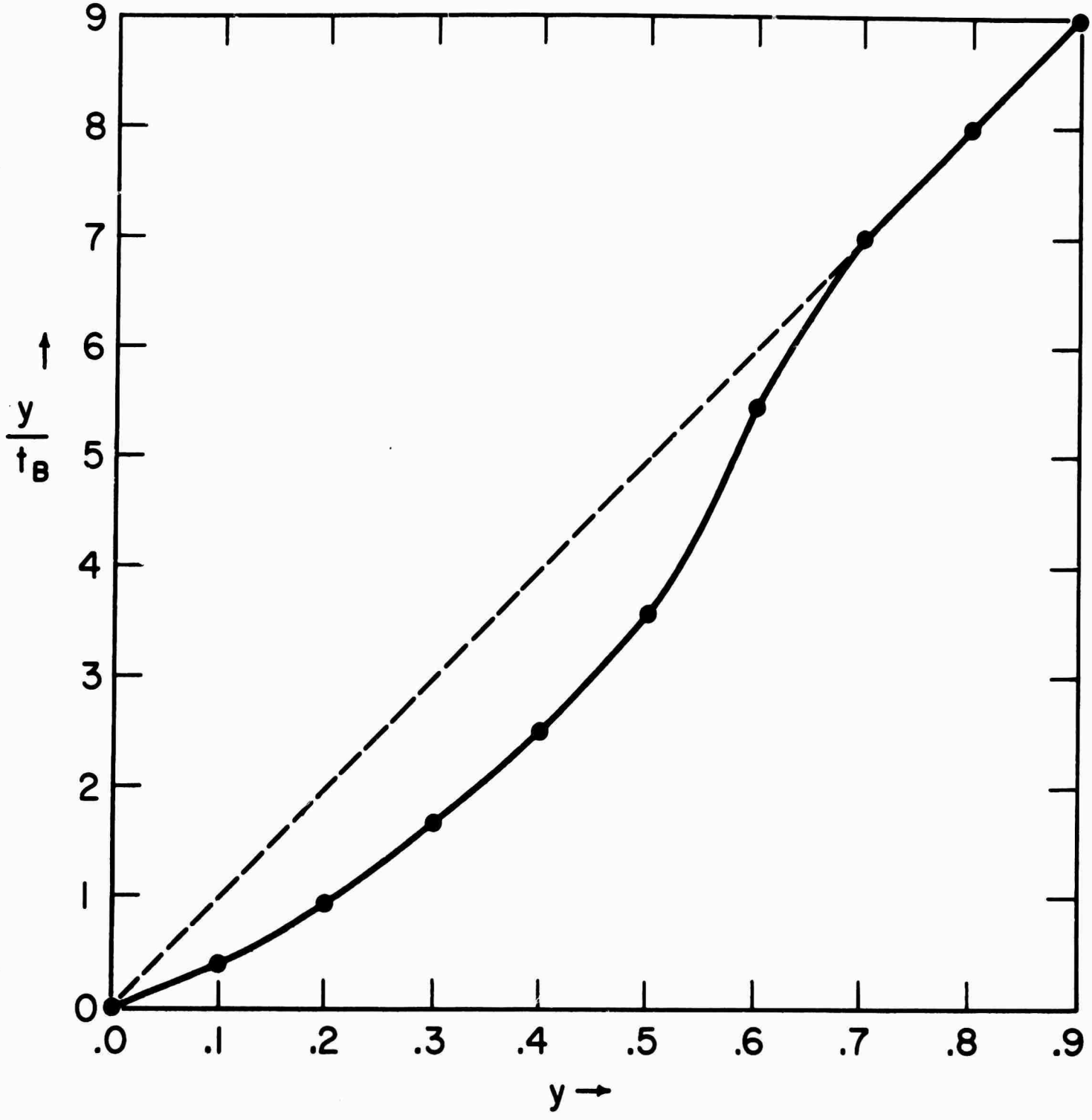
Figure 1. Typical transient current pulses excited by weak intensity strongly absorbed light incident upon anthracene (A), (B) and $As_2Se_3$ (C). Curve (C) is taken from Fig. 5 of ref. (3).

Figure 2. Plot of the current versus time multiplied by the voltage parameter y obtained from a Monte Carlo calculation for a system with $N_I = 1000$, $N_D = 7000$, $\tau_\alpha = \tau_\gamma = 4 \times 10^{-4}$, $\tau_\beta = 10^{-3}$, and $t_o = 10^{-3}$. The yt axis is in units of $t_o$.

Figure 3. Plot of $y/t_B$ versus y where $t_B$ is determined from the break in the current pulses as shown in Fig. 2.


(a)
i
(b)
i
(c)
i
t →


y = 2.5
y = 1.5
y = 0.9
y = 0.7
y = 0.5
y = 0.3
y = 0.1
$t_B$
i
0
1
2
3
4
5
yt


9
8
7
6
5
4
3
2
1
0
$\frac{y}{t_B}$ ↑
.0
.1
.2
.3
.4
.5
.6
.7
.8
.9
y →

# MONTE CARLO CALCULATIONS OF TRANSIENT PHOTOCURRENTS*

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Abstract

In this paper we show the results of a simple Monte Carlo calculation simulating transient photocurrents in low mobility material. We have applied these calculations to four different distributions of bulk traps for various temperatures and applied fields.

Recently[1] we have shown that using an elementary Monte Carlo approach we can calculate the main features of the experimentally observed transient photocurrent in low mobility material. These features include a long tail after the break point of the current pulse (which was assumed to be the arrival of the main burst of charge) and an apparent field dependence of the mobility. We assumed that bulk trapping, bulk trap release and surface trapping and release are all active.

In this paper we discuss the results of additional calculations including temperature and field dependence of the pulse for four different distributions of bulk traps. The four distributions are 1) single level,

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half gaussian centered at zero with a half width equal to half the single level energy of (1), 3) exponential with a characteristic energy equal to half the energy of (1), and 4) uniform with a cut-off at the single level of (1). The cross section of all traps was assumed to be the same.

In reference (1) we indicate the main features of the calculation. The duration of a particular trapping or trap release event is given by:

$$t_J(n) = -\tau_J \ln r_J(n) \qquad (1)$$

where $r_J(n)$ is a random number between 0 and 1 generated by the computer. In order to change temperatures it was only necessary to make those $\tau_J$'s which involve trap emptying processes temperature dependent. When there was a distribution of bulk traps the energy $E_n$ of the $n^{th}$ level that was filled by a particular trapping event was determined by a random number $r_n$ and the distribution function. For example for a uniform distribution, $E_n = 0.1\ r_n$, for an exponential distribution $E_n = -0.05 \ln r_n$ and for the simple gaussion $E_n = .05[-\ln r_n]^{1/2}$. The emptying time for any particular level was, of course, proportional to $\exp[E_n/kT]$.

We have assumed that 80% of the particles are initially trapped at the surface with trapping energy of 0.085 e.v. while the remainder are instantaneously released into the bulk. We have also used a least square fit to the calculated curve whenever possible to minimize fluctuation and reduce computer time.

In this short paper we cannot give all the detailed results of the calculation. To indicate some of the effects we show in Fig. 1 and 2 the current vs time curves for several voltages for the case of the single level trap at 200°K and 250°K. In Figure 3-5 we show the curves for the other

three distribution of traps at 200 °K. In most cases an apparent transit time indicated by the vertical arrow on the curves can be determined. The only exceptions are the low voltage curves in the case of the exponential distribution. From Fig. I-5, we see that there is an apparent field dependence of the mobility in the cases of the single level and gaussian distribution while in the uniform and exponential case no field dependence were found except perhaps at the lowest voltages. In Fig. 6 and 7 we show the reciprocal of the apparent transit time vs voltage for the single level and the gaussian case.

It is not hard to understand why the uniform and exponential distributions exhibit almost no field dependence over the range of temperatures considered. When there are relatively few trapping events, the drift is determined by the emptying time of the more probable trapping level. For the distributions used, the more probable levels are at very low energy and emptying does not appreciably slow down the carriers at these temperatures. We have calculated the drift for the uniform distribution at 125°K. We did see a field dependence here because even the shallow levels have a long emptying time. Also at very much lower voltages than those considered here, the number of trapping events becomes very large and one would expect that the drift would be determined by the very deep levels where emptying is slow. In this case one should again observe an apparent field dependence. These calculations have not as yet been tried although the lowest voltage curve for the exponential case seems to bear this out.

Finally, for the cases of the single level trap and the gaussian we show in Figs. 8 and 9 the log of the break point vs the log of the voltage for several temperatures. As expected the lower temperatures show a faster

dependence of the transit time on voltage than the higher temperatures. This is similar to what Tabak[2] found in amorphous selenium and Scharfe[3] in $As_2Se_3$.

To date, the main conclusion that we draw from these calculations is that unless the idealized pulse shape is obtained in an experiment, deriving information on the transport parameters is very tenuous. For pulses with long tails one must make a careful study of the transit time as a function of field, temperature, and thickness (magnitude of transit time) of the material.

## References

1. M. Silver, K. S. Dy and I. L. Huang, Phys. Rev. Letters 27, 21 (1971).
2. M. D. Tabak, Phys. Rev. 32, 2104 (1970).
3. M. E. Scharfe, Phys. Rev. B2, 5025 (1970).

## FIGURE CAPTIONS

Figure 1. Current vs time. The unit of time for each curve was $10^{-3}/y$ sec. The trapping time was $4 \times 10^{-4}$ sec. The trap emptying time for bulk traps was $10^{-3}$ sec at 200°K and for the surface traps was $4 \times 10^{-4}$ sec. This curve was obtained without a least square fit. y is a parameter proportional to the applied voltage.

Figure 2. Current vs time. The unit of time for each curve was $10^{-3}/y$ sec. A least square fit was used. y is a parameter proportional to the applied voltage.

Figure 3. Current vs time. The unit of time for each curve was $10^{-3}/y$ sec. A least square fit was used. y is a parameter proportional to the applied voltage.

Figure 4. Current vs time. The unit of time for each curve was $10^{-3}/y$ sec. A least square fit was used. y is a parameter proportional to the applied voltage.

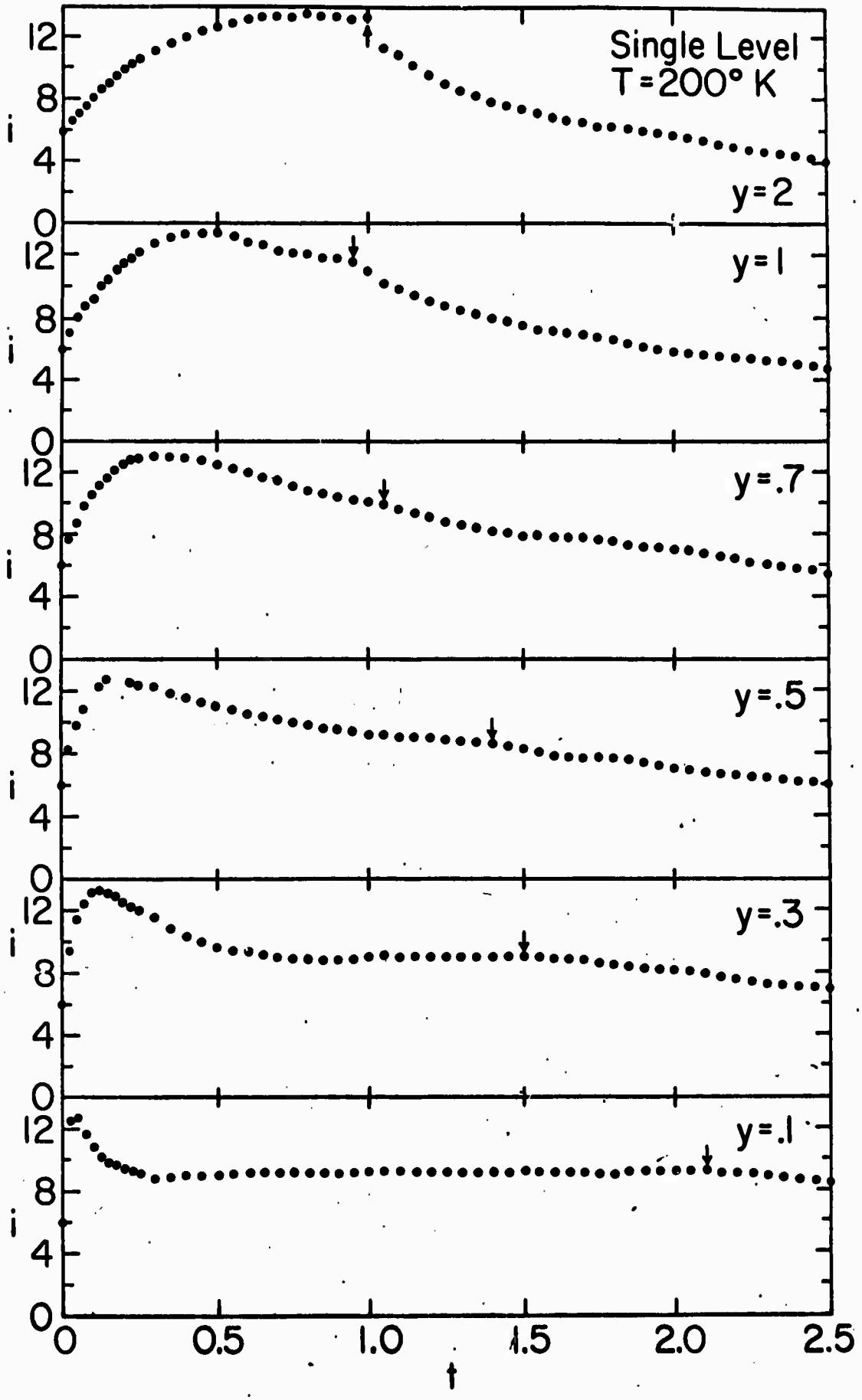
Figure 5. Current vs time. The unit of time for each curve was $10^{-3}/y$ sec. A least square fit was used. y is a parameter proportional to the applied voltage.

Figure 6. Reciprocal of the apparent transit time $t_B/y$ vs y.

Figure 7. Reciprocal of the apparent transit time $t_B/y$ vs y.

Figure 8. Log-log plot of the reciprocal of the apparent transit time vs y. (The 300°K curve has been displaced slightly for clarity.)

Figure 9. Log-log plot of the reciprocal of the apparent transit time vs. y.


Single Level
T=200° K
y=2
y=1
y=.7
y=.5
y=.3
y=.1
i
t
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1.0
1.5
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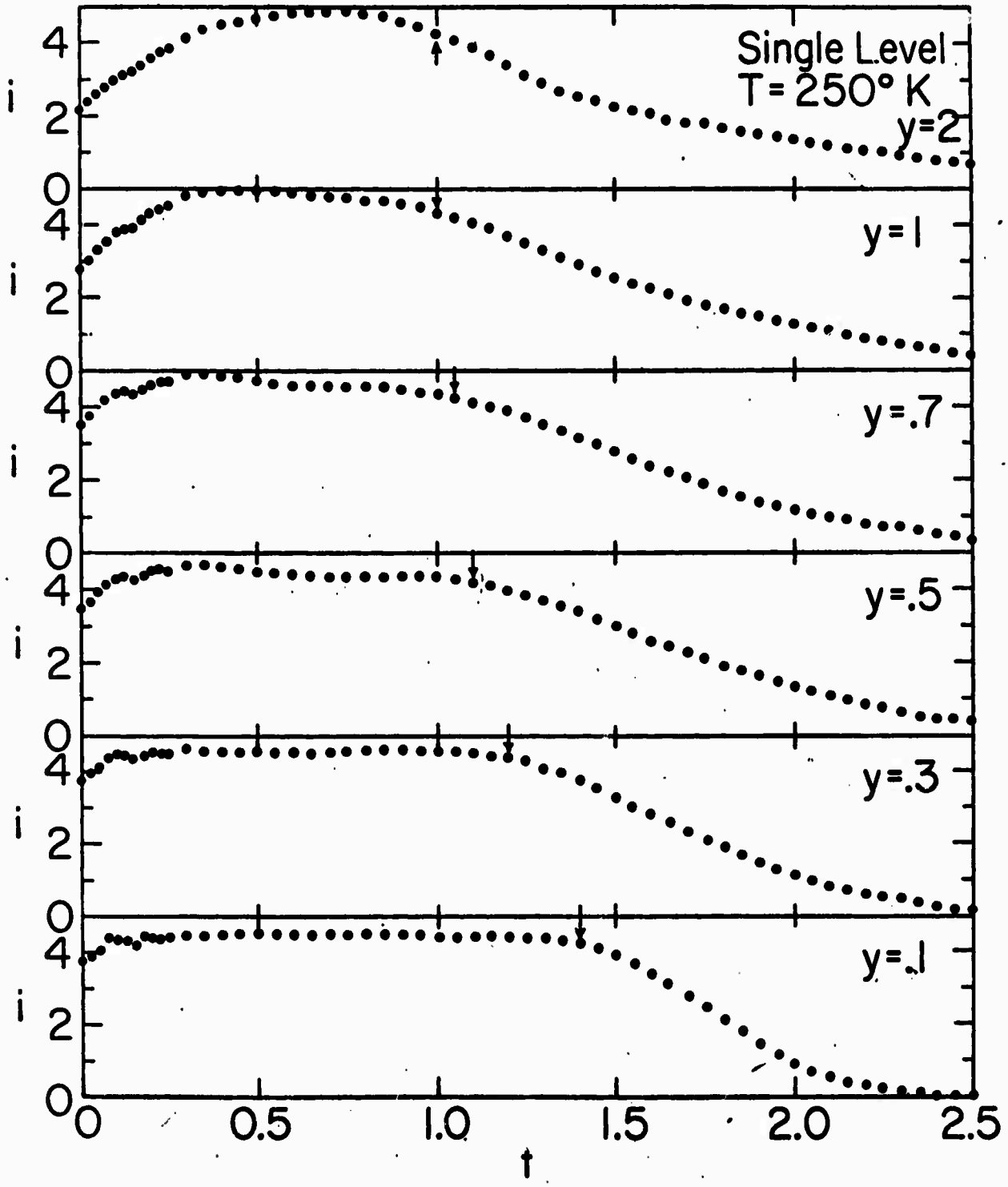
2.5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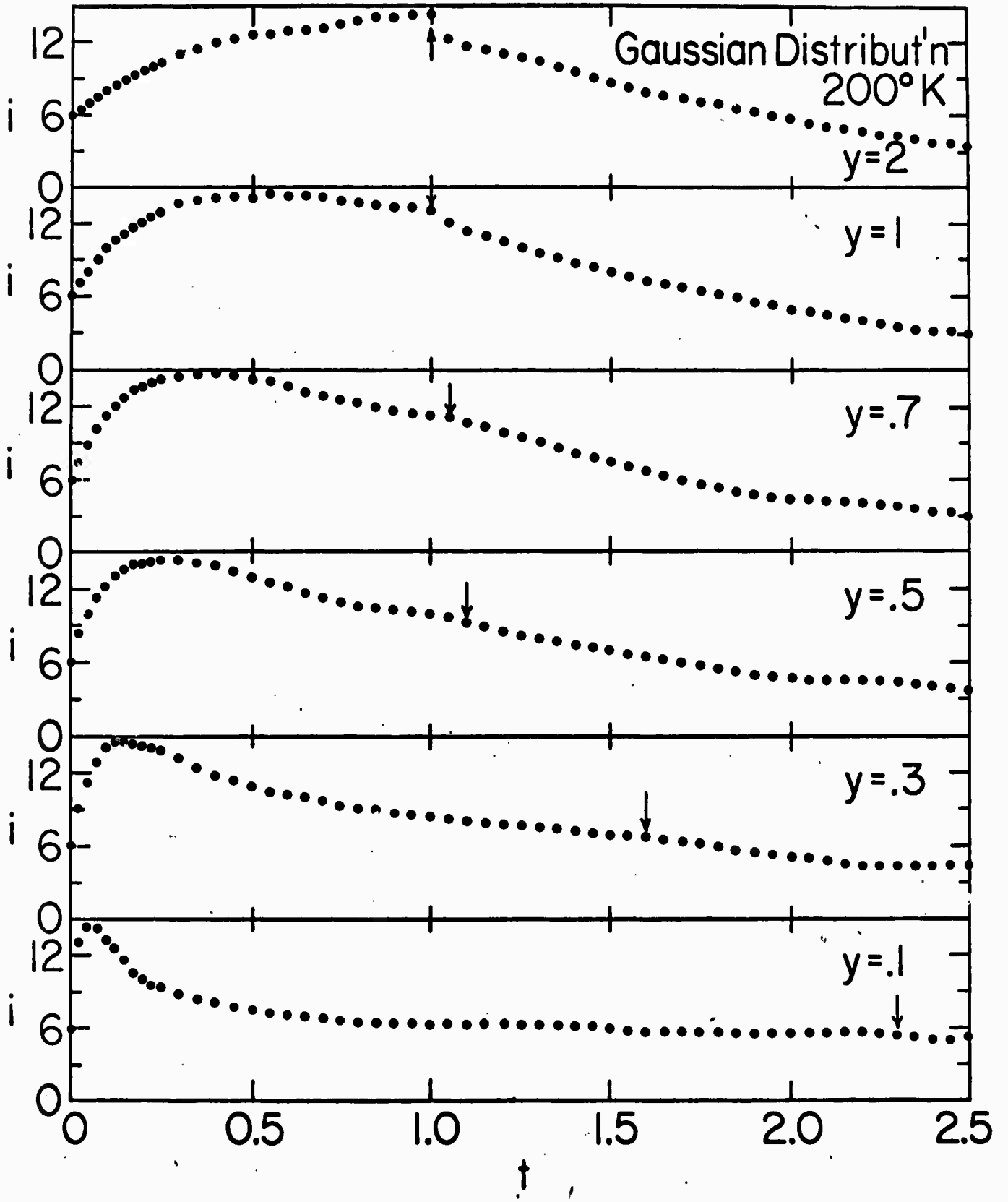
Gaussian Distribut'n
200° K
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y=1
y=.7
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y=.1
i
12
6
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0
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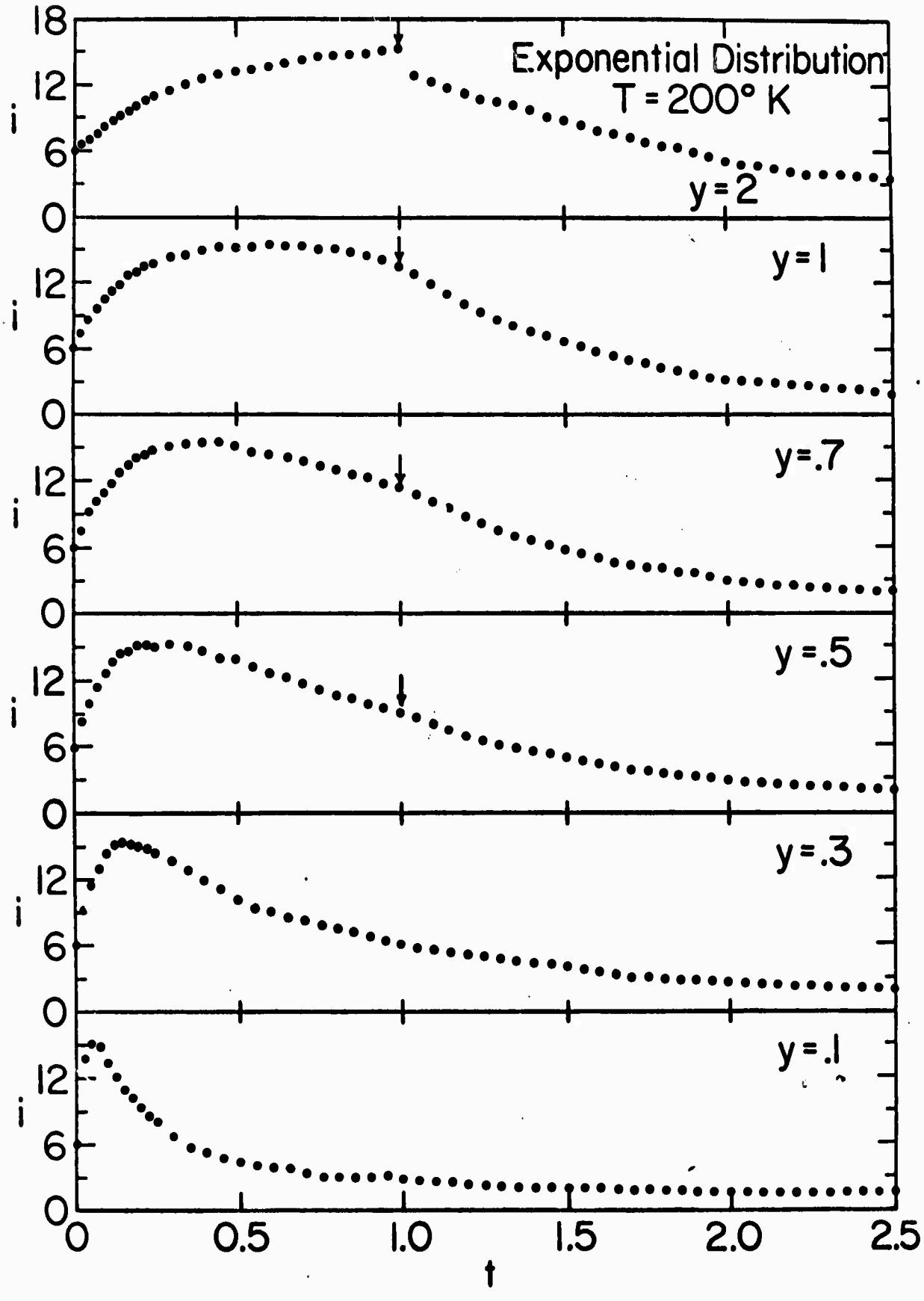
1.5
2.0
2.5
t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y = .5
y = .3
y = .1
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1.0
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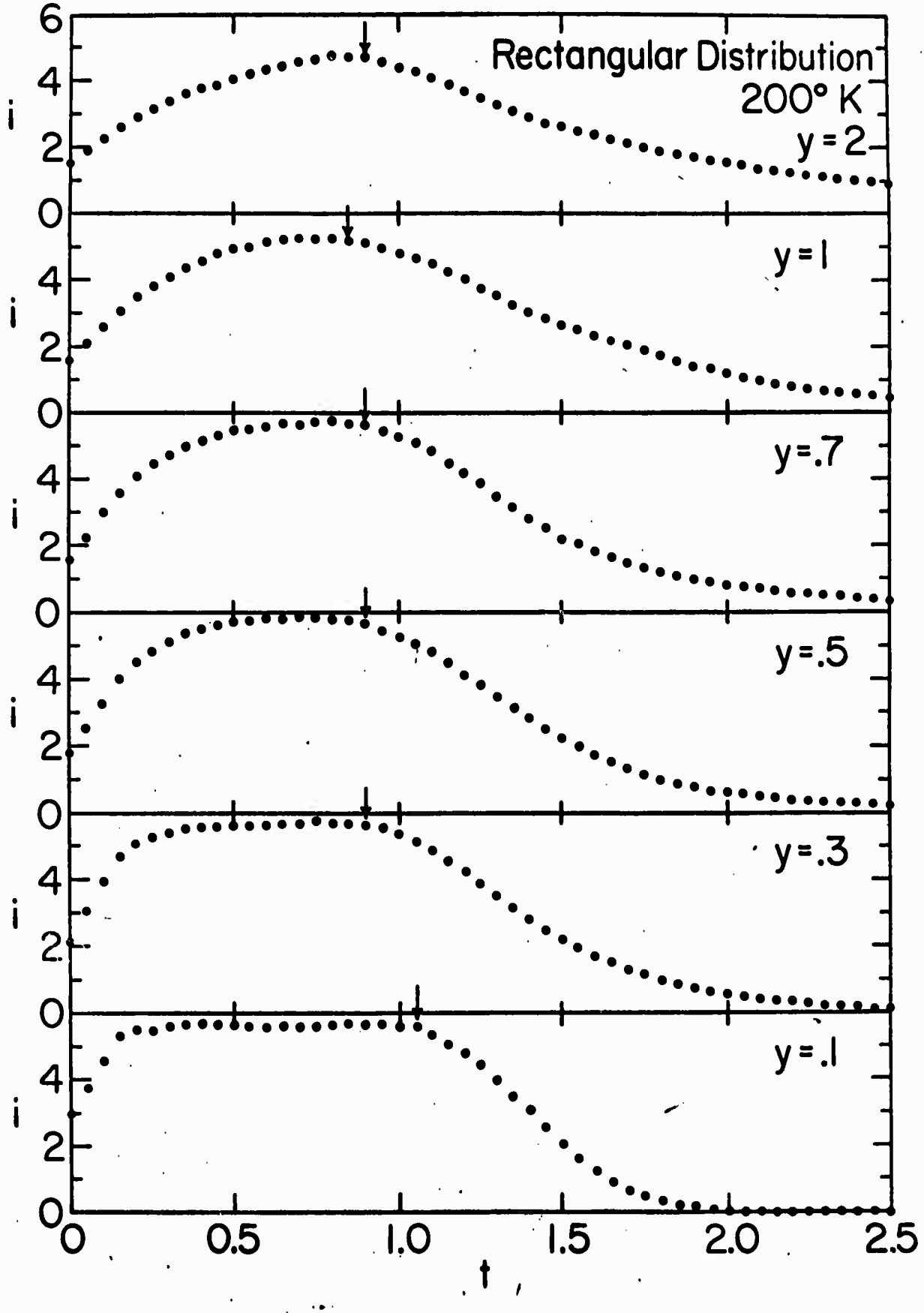
2.0
2.5
t


Rectangular Distribution
200° K
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y = 1
y = .7
y = .5
y = .3
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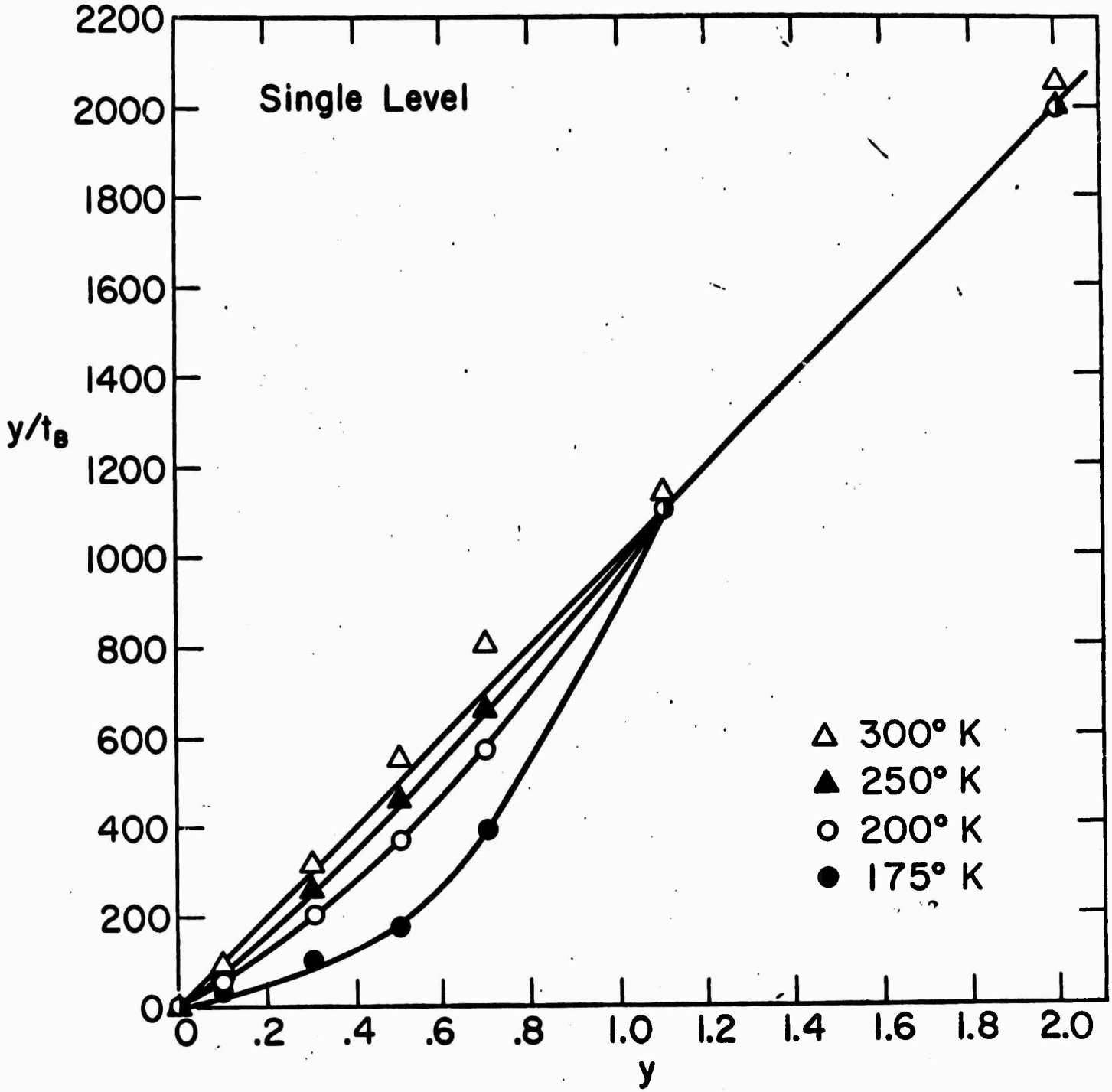
2
4
6


Single Level
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1800
1600
1400
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600
400
200
0
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.4
.6
.8
1.0
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1.4
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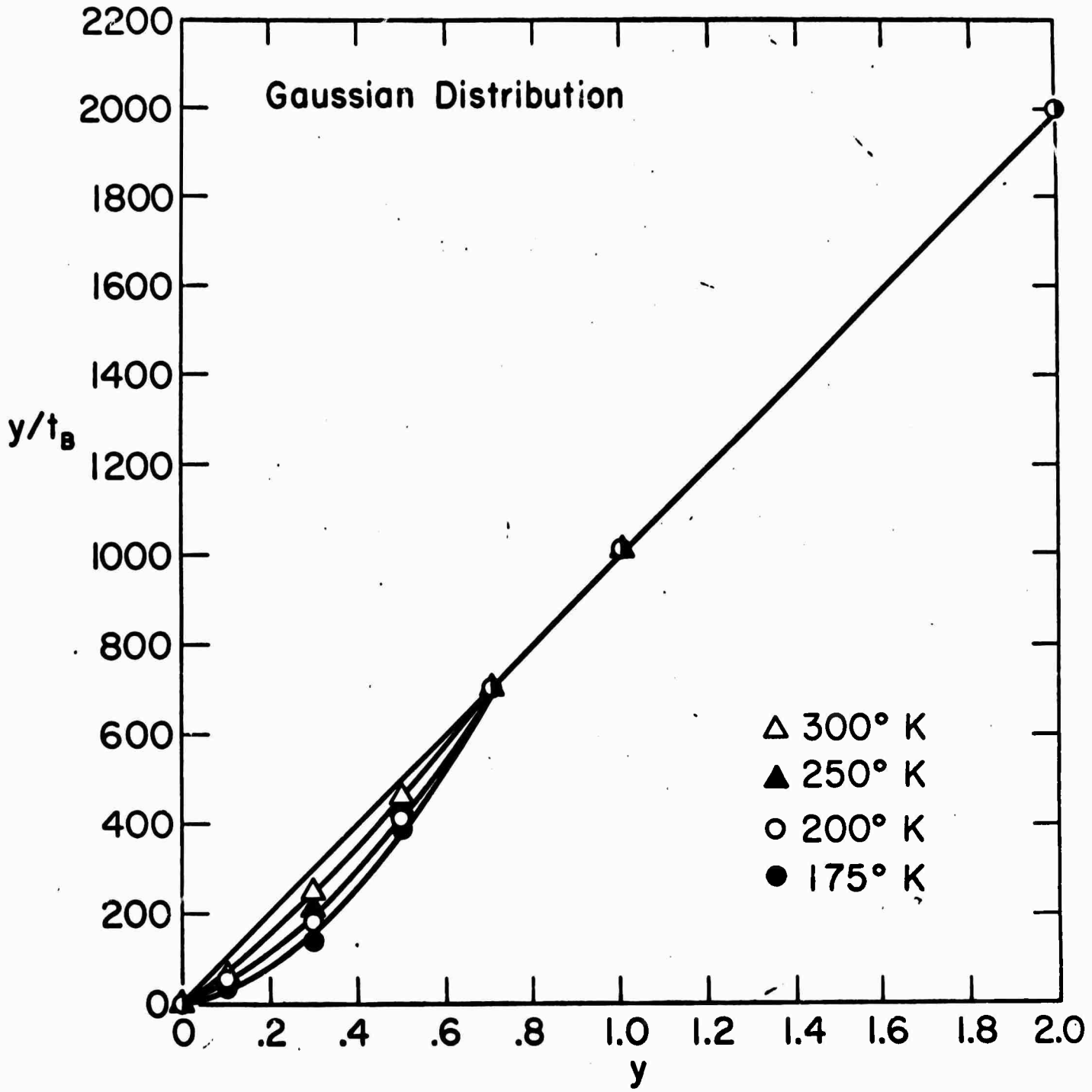
1.8
2.0
y
△ 300° K
▲ 250° K
○ 200° K
● 175° K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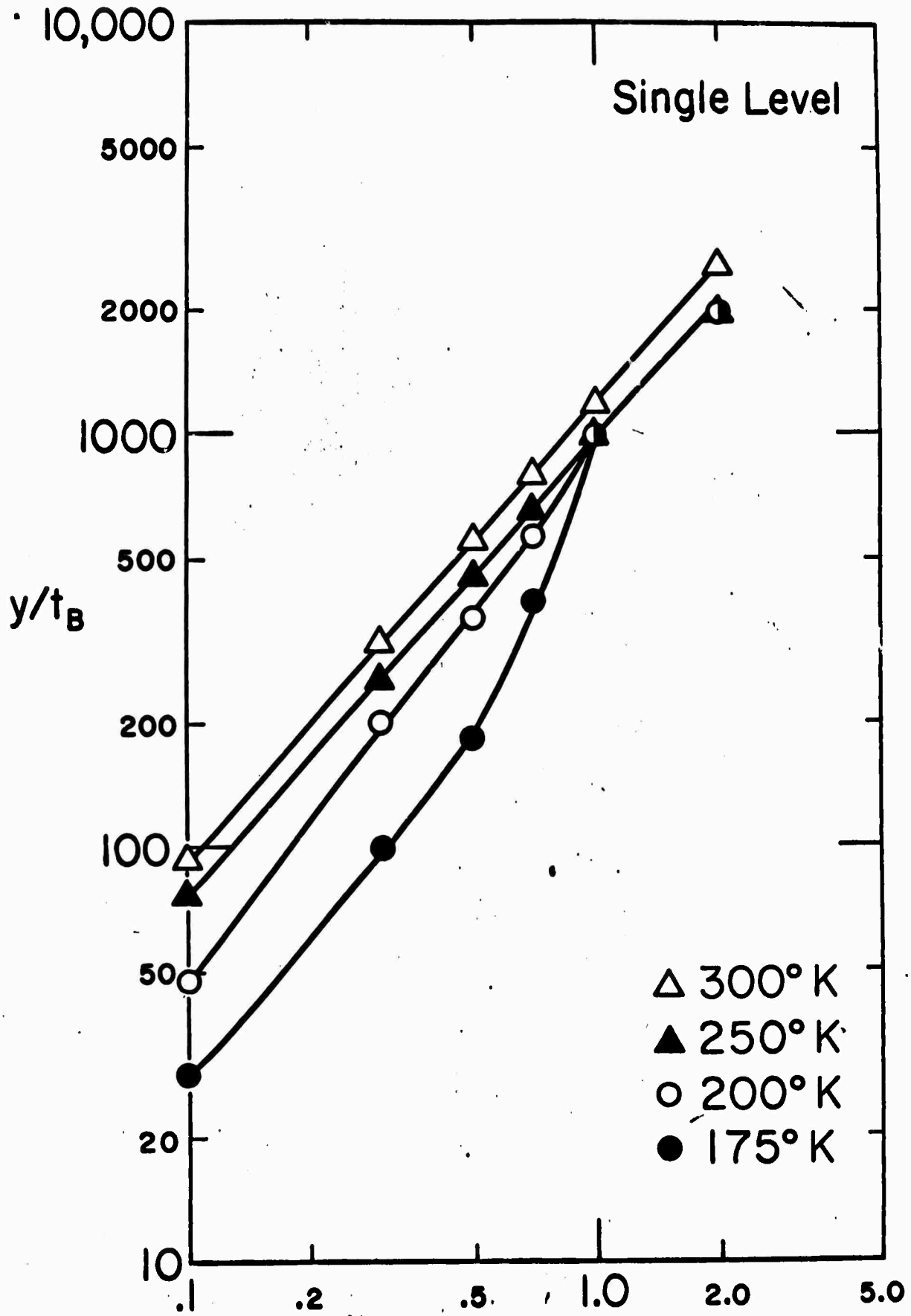
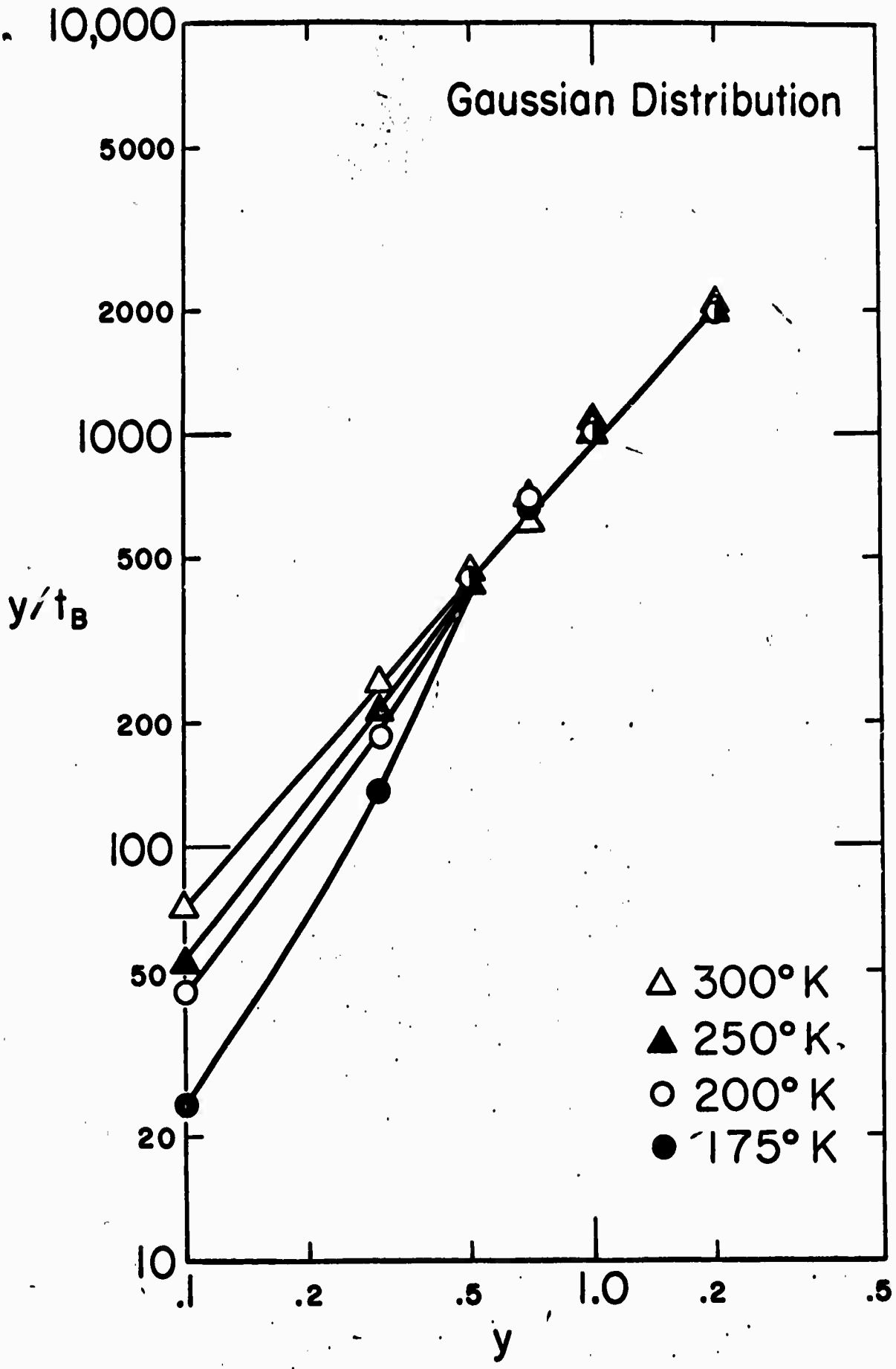
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
y
△ 300° K
▲ 250° K
o 200° K
● 175° K


Single Level
10,000
5000
2000
1000
500
200
100
50
20
10
$y/t_B$
.1
.2
.5
1.0
2.0
5.0
△ 300° K
▲ 250° K
○ 200° K
● 175° K


Gaussian Distribution
10,000
5000
2000
1000
500
200
100
50
20
10
y/t_B
.1
.2
.5
1.0
.2
.5
y
△ 300° K
▲ 250° K
○ 200° K
● 175° K